

**Nonequilibrium Thermodynamics. Symmetric and Unique  
Formulation of the First Law, Statistical Definition of Heat and  
Work, Adiabatic Theorem and the Fate of the Clausius  
Inequality: A Microscopic View**

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## Abstract

The status of heat and work in nonequilibrium thermodynamics is quite confusing and non-unique at present with conflicting interpretations even after a long history of the first law  $dE(t) = d_eQ(t) - dW_e(t)$  in terms of exchange heat and work, and is far from settled. Moreover, the exchange quantities lack certain symmetry (see text). By generalizing the *traditional* concept to also include their time-dependent irreversible components  $d_iQ(t)$  and  $d_iW(t)$  allows us to express the first law in a symmetric form  $dE(t) = dQ(t) - dW(t)$  in which  $dQ(t)$  and work  $dW(t)$  appear on equal footing and possess the symmetry. We prove that  $d_iQ(t) \equiv d_iW(t)$ ; as a consequence, irreversible work turns into irreversible heat. Statistical analysis in terms of microstate probabilities  $p_i(t)$  *uniquely* identifies  $dW(t)$  as *isentropic* and  $dQ(t)$  as *isometric* (see text) change in  $dE(t)$ , a result known in equilibrium. We show that such a clear separation does not occur for  $d_eQ(t)$  and  $dW_e(t)$ . Hence, our new formulation of the first law provides tremendous advantages and results in an extremely useful formulation of non-equilibrium thermodynamics, as we have shown recently [Phys. Rev. E **81**, 051130 (2010); *ibid* **85**, 041128 and 041129 (2012)]. We prove that an adiabatic process does not alter  $p_i$ . *All these results remain valid no matter how far the system is out of equilibrium.* When the system is in internal equilibrium,  $dQ(t) \equiv T(t)dS(t)$  in terms of the instantaneous temperature  $T(t)$  of the system, which is reminiscent of equilibrium, even though, neither  $d_eQ(t) \equiv T(t)d_eS(t)$  nor  $d_iQ(t) \equiv T(t)d_iS(t)$ . Indeed,  $d_iQ(t)$  and  $d_iS(t)$  have very different physics. We express these quantities in terms of  $d_e p_i(t)$  and  $d_i p_i(t)$ , and demonstrate that  $p_i(t)$  has a form very different from that in equilibrium. *The first and second laws are no longer independent so that we need only one law, which is again reminiscent of equilibrium.* The traditional formulas like the Clausius inequality  $\oint d_eQ(t)/T_0 < 0$ ,  $\Delta_e W < -\Delta [E(t) - T_0 S(t)]$ , etc. become equalities  $\oint dQ(t)/T(t) \equiv 0$ ,  $\Delta W = -\Delta [E(t) - T(t)S(t)]$ , etc, a quite remarkable but unexpected result in view of the fact that  $\Delta_i S(t) > 0$ . We identify the uncompensated transformation  $N(t, \tau)$  during a cycle. We determine the irreversible components in two simple cases to show the usefulness of our approach; here, the traditional formulation is of no use. Our extension bring about a very strong parallel between equilibrium and non-equilibrium thermodynamics, except that one has irreversible entropy generation  $d_i S(t) > 0$  in the latter.

## I. INTRODUCTION AND CONTROVERSY

### A. Heat and Work

Gislason and Craig [1] recently remarked that the definition of work in nonequilibrium "...thermodynamics processes remains a contentious topic," a rather surprising statement, as the field of thermodynamics is an old discipline. However, there is some truth to their critique, which was motivated by an earlier paper by Bertrand [2], who revisited the confusion first noted by Bauman [3] about different formulation of work [the *exchange heat work*  $d_e W(t) = P_0 dV(t)$  or the *generalized work*  $dW(t) = P(t)dV(t)$ , see Refs. [4–10] and below] in terms of the external ( $P_0$ ) and instantaneous or internal ( $P(t)$ ) pressures [11] at a given instant  $t$ , see Fig. 1, and discussed by many others [12–33] since then with no consensus [12, p.181, Vol. 1]. Traditional formulation of nonequilibrium statistical mechanics and thermodynamics [34, 35] follows a mechanistic approach in which the system of interest follows its (classical or quantum) mechanical evolution in time. Being a mechanical concept, work is easier to identify in thermodynamics than heat; the latter is not possible to be identified with any mechanical force. Therefore, one usually identifies heat by first identifying work and then subtracting the latter from the energy change [34] in the first law. This means that different formulations of work will result in different heats. We refer the reader to the above references for an interesting history of the confusion. Gislason and Craig [29] list twenty-six representative textbooks including [36, 37] where the pressure-volume work and heat are defined so differently that they are not equivalent in the presence of irreversibility, and there appears to be no consensus about their right formulation so far; see the recent debate in the field [17, 21–26]. Unfortunately, none of the latter sources consider *internal variables* [7, 8, 38, and references therein] that are needed to describe irreversible processes but do not appear explicitly in the Hamiltonian. They also do not consider *thermodynamic forces* [6–8] that are non-zero when the system is away from equilibrium.

The attempt to define heat by first defining work leaves the concept of heat devoid of clear physical significance, especially since it depends on what we mean by work. In many cases, work is identified by considering the work performed by bodies external to the system (the medium; see Fig. 1), which may have nothing to do with the work done by the system, especially when we consider irreversible processes. This has created a lot of confusion in the

literature when dealing with irreversible processes; see Refs. [17, 21–26] for a recent discussion; see also [10]. The traditional formulation of statistical mechanics and thermodynamics [34, 35] follows a mechanistic approach in which the system of interest, to be precise its microstate, follows its (classical or quantum) mechanical evolution in time. The only difference between mechanics and thermodynamics is that the evolution in thermodynamics is *always* stochastic, which makes the evolution irreversible in accordance with the second law; see for example a recent review [39]. Therefore, it is crucial to consider a *statistical foundation* of nonequilibrium thermodynamics for a better understanding of heat and work, a project we have also initiated recently [7–9, 39, 40]. The concept of work follows in a trivial manner by taking (a *stochastic average* of) its mechanical analog (work done by generalized forces in the Hamiltonian formulation) [34]. and was shown to be given by  $dW_V(t) = P(t)dV(t)$  for the pressure work; see Ref. [7]. These forces can be controlled by an observer and determine the *observables* in the system; see for example [7, 8]. It was shown in Ref. [7, 8] that the first law can *also* be written in terms of the *generalized heat*  $dQ(t)$  *added to* and the *generalized pressure work*  $dW(t)$  *done by* the system:

$$dE(t) = dQ(t) - dW(t), \quad (1)$$

where

$$d_i Q(t) \equiv dQ(t) - d_e Q(t), d_i W(t) \equiv dW(t) - d_e W(t), \quad (2)$$

denote irreversible heat and work, respectively, generated within the system [4]. However, the interpretation of the above new formulation, its statistical basis, and its relationship with the traditional formulation  $dE(t) = d_e Q(t) - d_e W(t)$  in terms of exchange heat  $d_e Q(t) = T_0 d_e S(t)$  and work  $d_e W(t) = P_0 dV(t)$  was not explored in earlier publications [7–10].

For an isolated system, the mechanical observables, collectively denoted by the set  $\mathbf{X}$ , are additive integrals of motion [34, 41] such as the energy  $E$ , the number of particles  $N_j$  of different species, and linear and angular momenta  $\mathbf{P}$  and  $\mathbf{M}$  of the system, respectively, whose values depend on the preparation of the system. When the motion is confined to a finite region of space, the volume  $V$  of this region also characterizes the system as a constraint. The *constraints* are also treated as observables. The internal variables unfortunately cannot be controlled by an observer. Despite this, the concept of work needs to incorporate the additional work required in changing the internal variables. This gives rise to some complication in identifying the form of work associated with them. The collection of ob-

servables and internal variables will be called *state variables* and will be denoted by the set  $\mathbf{Z}$ . The macrostate can be characterized in a larger state space of  $\mathbf{Z}$ , even though the observed macrostate is characterized by  $\mathbf{X}$ . The internal variables do not remain constant for an isolated system as the system relaxes. In this sense, we must treat the isolated system as interacting with an appropriate "fictitious" medium to allow for the variation of internal variables, a fact not emphasized in the literature to the best of our knowledge; see Ref. [8]. As both energy and work are mechanical concepts, it is trivial to identify their statistical averages over microstates whether the system is in or out of equilibrium.

## B. Controversy

As the concept of heat has no analog in mechanics, it is usually identified indirectly as that energy change which is *not* work. *This kind of approach makes heat and work not unique*: a change in one affects the other; only their difference has a well-defined meaning. This has created a lot of confusion in the field. Our goal in this work is to establish that there exists a consistent procedure in which the partition is *unique* so that work and heat are no longer arbitrary in irreversible processes. They are given by generalized work and heat despite the controversy. The first law of thermodynamics, see for example, Refs. [6, 34], is a very general statement and is supposed to be valid for all processes, and not just equilibrium processes. The traditional formulation of the first law in terms of the *exchange heat and work* is not only oblivious to the internal variables and thermodynamic forces, whose presence must control the approach to equilibrium, but most significantly, is also oblivious to the violation of the second law; see below. This is why we need to use both the first and the second laws in nonequilibrium thermodynamics. How can a formulation of a fundamental law of physics allow for the violation of another fundamental law of physics? There is also an asymmetry between heat and work that will be elaborated below in that the two terms are not on an equal footing. There is obviously no problem for reversible processes.

We mostly consider mechanical work including dissipation, but the arguments are valid for all kinds of work; see Sec. VIII, however. Zemansky [37, p.73] defines heat as energy exchange "...by virtue of a temperature difference only." Unfortunately, this rules out any isothermal heat exchange and cannot be considered general. Kirkwood and Oppenheim define heat as energy exchange resulting in "...the temperature increment..." (which rules out

phase changes requiring latent heat) and later note that the work may be converted to heat due to frictional dissipation [36, pp. 16,17] as was first observed by Count Rumford in 1798 during the boring of cannon [6]. These are two of the examples where heat is defined directly without first identifying work; they have limitations and cannot be considered general, especially when irreversibility is present. The situation with work is just as confusing as we noted above with its two different formulations:  $d_e W(t) = P_0 dV(t)$  or  $dW(t) = P(t)dV(t)$ .

Dissipation always gives rise to positive entropy generation due to irreversibility and also raises the temperature such as due to friction or the Joule heat in resistors. Therefore, it is natural to account for such viscous dissipation in work and heat when dealing with nonequilibrium systems, as they are integral to the system and dictate its relaxation. The fact that literature is not very clear on how to incorporate viscous dissipation has motivated this work; see however [31, 33], but the authors do not take the discussion far enough to obtain the results derived here. Recently, dissipative forces are explicitly considered in stochastic trajectory thermodynamics [15, 17–27]. However, the approach differs from our approach [42] in important ways and has also given rise to controversy, and remains contentious [17, 21–26]. In addition, the approach is not general as it is limited to isothermal variations and to cases where Langevin dynamics is applicable; see, however, Hoover and Hoover [43] where an example of a time-reversible deterministic Hamiltonian system is given.

### C. New Results

We interpret heat and work used in the recent reformulation in Eq. (1) that was proposed in Refs. [7–9] and follow the consequences with an aim to develop their statistical definition. The formulation makes the first law identical to the second law (in the guise of the Gibbs fundamental relation) In general,  $d_e Q(t) \equiv T_0 d_e S(t)$ , but  $dS(t)$  and  $dQ(t)$  are not related to each other, except in internal equilibrium [7]. Moreover, it would be incorrect to conclude from  $dS(t) \equiv d_e Q(t)/T_0 + d_i S(t)$  that  $d_i Q(t) = T_0 d_i S(t)$ ; see later. The aim of any theory of nonequilibrium thermodynamics is to determine the entropy change  $dS(t)$ . Therefore, the determination of  $d_i S(t)$  becomes the focus in any investigation of a body in the traditional formulation. The second law is reflected in the inequality  $d_i S(t) > 0$  for any irreversible process. The statistical analysis provides an elegant formulation of nonequilibrium thermodynamics in which there is a *unique* and *natural* distinction between nonequilibrium work

and heat in that the generalized work represents *isentropic change in the (internal) energy* and the generalized heat represents the *isometric* (constant extensive state variables excluding the energy) change in the energy. The latter change results purely from the entropy change. The unique partition of energy remains valid no matter how far the system is out of equilibrium. The assumption of *internal equilibrium* allows us to express the first law in terms of the *instantaneous* (or internal) fields. This brings about a very close parallel between nonequilibrium and equilibrium processes such as  $dS(t) \equiv dQ(t)/T(t)$  and the existence of a theorem for irreversible processes identical in spirit to the *adiabtic theorem* [34] for equilibrium processes. The approach proposed recently in Refs. [7–9, 39] deals directly with  $dS(t)$  without a need to use  $d_e S(t)$  and  $d_i S(t)$  separately, although they can also be evaluated in our approach. Therefore, our approach should be quite useful as the entropy is a state variable; see below, however, for other advantages. A particular symmetry is explicitly seen in our formulation in that both  $dQ$  and  $dW$  not only do not change with the nature of the process but also exhibit an identical formulation in terms of entropy and volume, respectively. In other words, they are found to be on an equal footing. As a consequence, the first law becomes identical to the second law (as the Gibbs fundamental relation) so we only deal with a single law. The Clausius inequality [44] turns into an equality in *all* cases as  $dQ(t)/T(t)$  becomes a state variable, the work is expressed as an equality, as if we are dealing with equilibrium processes, a quite remarkable result in its own right, even though there is irreversible entropy generation. It has been recently suggested [32] that the use of internal fields is not always consistent with the second law. We find no such problem in our approach.

The new formulation of the first law contains not only the observables and the instantaneous fields of the system but also explicitly contains internal variables so no information about the system is lost. This makes the new formulation quite beneficial. The instantaneous temperature, pressure, etc. of the system need not be identical to those of the medium when the system is out of equilibrium with the medium as has become clear recently [7, 16, 45]. Thus, our approach also overcomes the objection raised by Cohen and Mauzerall [21] against the stochastic trajectory thermodynamics [15, 17, 27] to which our approach is easily extended. We will establish that there are several benefits in accounting for viscous dissipation within the system in the first law, but care must be exercised. Our approach, which *assumes* the existence of entropy even for nonequilibrium states [39] as

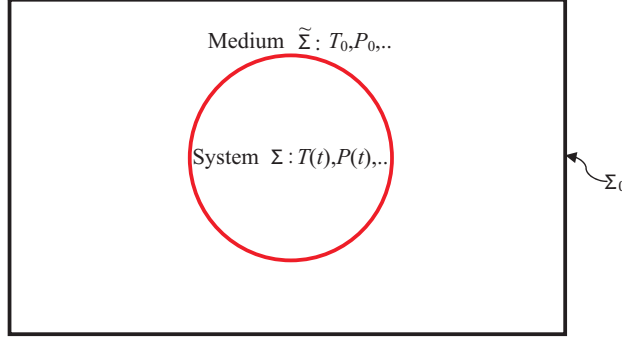


FIG. 1: Schematic representation of  $\Sigma$ ,  $\tilde{\Sigma}$  and  $\Sigma_0$ . We assume that  $\Sigma$  and  $\tilde{\Sigma}$  are homogeneous and in internal equilibrium, but not in equilibrium with each other. The internal fields  $T(t), P(t), \dots$  of  $\Sigma$  and  $T_0, P_0, \dots$  of  $\tilde{\Sigma}$  are not the same unless they are in equilibrium with each other. There will be viscous dissipation in  $\Sigma$  when not in equilibrium with  $\tilde{\Sigma}$ .

was first proposed by Clausius [44], is otherwise very general as we do not restrict ourselves to any particular dynamics and to only isothermal variations. It allows us to incorporate viscous dissipation, due to the presence of thermodynamic forces and internal variables, in the discussion explicitly within this general framework. We consider our system  $\Sigma$  (see Fig. 1) surrounded by a very large medium  $\tilde{\Sigma}$  so large that its fields such as its temperature  $T_0$ , pressure  $P_0$ , etc. are not affected by the system. They form an isolated system  $\Sigma_0$ . We consider all systems to be stationary; their relative motion will be considered only in Sec. VII. The surface separating  $\Sigma$  and  $\tilde{\Sigma}$ , which may represent a piston, will be treated as having no interesting thermodynamics of its own although it may participate in irreversibility due to field (such as temperature, pressure, etc.) differences across it. Because of the enormous size of the medium with respect to that of the system, all irreversible components in  $\Sigma_0$  appear within  $\Sigma$  ( $d_i Q(t) \equiv d_i Q_0(t)$ ,  $d_i W(t) \equiv d_i W_0(t)$ ) although this is not always so in the literature [46]. The situation of finite surroundings has been considered by Bizarro [31] and by us in Ref. [8].) In the following, all extensive quantities pertaining to  $\tilde{\Sigma}$  and  $\Sigma_0$  carry an annotation tilde or a suffix 0, respectively, and those pertaining to  $\Sigma$  carry no suffix. We will use *body* to refer to any one of the above three systems and use symbols without any suffix to denote its quantities.

Our discussion is easily extended to the case when  $\tilde{\Sigma}$  is comparable to  $\Sigma$  in size, as is easily seen in Secs. VII and IX, and Ref. [8]. In this case, we will refer to  $\tilde{\Sigma}$  as the surroundings,



whose fields will also change with time. However, to keep the discussion simple, we will treat  $\tilde{\Sigma}$  as an extensively large medium for the most part.

The layout of the paper is as follows. We briefly review the traditional formulation of the first law, its lack of symmetry, confusion and its limitations in the next section. In Sec. III, we follow our newly developed nonequilibrium thermodynamics and unravel the significance of heat and work in that approach. Several important results are derived there in the forms of theorems. Some of the results were announced earlier in Ref. [10] but have now been expanded. In Sec. IV, we argue that only the generalized work is consistent with the second law. The statistical definition of heat and work is taken up in Sec. V, which forms the core of the present work, where we show that this definition is identical with heat and work discussed in Sec. III and used in the earlier work [7–9]. This section also contains many important results including the adiabatic theorem for irreversible processes. A general expression for microstate probabilities is derived here, which clearly shows nonequilibrium effects in their formulation. We partition microstate probability changes into external and internal parts  $d_e p_i(t), d_i p_i(t)$  to obtain the statistical formulations for  $d_e Q(t), d_i Q(t)$  etc. We use the example of an ideal quantum gas to show how  $d_e p_i(t), d_i p_i(t)$  can be computed. In the following section, we discuss the Clausius inequalities (there are two different ones) and the Clausius equality and the work equality. In Sec. VII, we consider two applications of our formulation, where the traditional formulation cannot be applied. In Sec. VIII, we extend our discussion to include an additional observable. The results derived here are used in Sec. IX to study a closed system which is allowed to exchange some kind of "work" with a thermally isolated external object. This is a classic prototype model studied extensively; see for example, Ref. [34]. The last section contains a brief summary of results and a list of benefits of our approach.

## II. TRADITIONAL FORMULATION OF THE FIRST LAW

### A. Traditional Formulation

To truly appreciate our contribution, it is useful to consider how the first law is traditionally expressed. We will only consider a single internal variable  $\xi$  for simplicity. Similarly, we will consider only  $E$  and  $V$  for simplicity as observables with the number of particles  $N$  (only

a single species) held fixed, unless noted otherwise. Other variables are easy to include in the approach as we do in Sec. VIII. Traditionally,  $dQ(t)$  represents the amount of heat exchange  $d_e Q(t)$ , so that  $-dW(t)$  is identified with the work exchange  $-d_e W(t) \equiv d\tilde{W}(t) = P_0 d\tilde{V}(t)$  by the medium to the system, giving  $d_e W(t) = P_0 dV(t)$ . This is true even if the system cannot be assigned any pressure or if its *instantaneous* pressure  $P(t)$  is different from  $P_0$ . As the net heat exchange  $d_e Q(t) + d_e \tilde{Q}(t) = 0$ , we immediately verify  $d_e Q(t) \equiv T_0 d_e S(t)$ . There is no such general relation relations for other heats:  $dQ(t) \neq T_0 dS(t)$  and  $d_i Q(t) \neq T_0 d_i S(t)$ . The traditional formulation of the first law for a general process reads

$$dE(t) \equiv d_e Q(t) - d_e W(t) \equiv T_0 d_e S(t) - P_0 dV(t) \quad (3)$$

expressed in terms of either exchange quantities or external fields of  $\tilde{\Sigma}$ . Only when the process is reversible that we have  $dE(t) \equiv T_0 dS(t) - P_0 dV(t)$ . The external fields are conjugates to the observables in  $\tilde{\mathbf{X}}(\tilde{E}, \tilde{V})$ , with the medium affinity  $A_0$  conjugate to  $\tilde{\xi}$  vanishing. Thus, the above formulation of the first law is, as said earlier, oblivious to the internal variables and will not be considered when using this formulation. The following inequality for a cycle, commonly known as the *Clausius inequality*, follows from  $dS > d_e Q(t)/T_0$ ,

$$\oint d_e S(t) \equiv \oint d_e Q(t)/T_0 < 0, \quad (4)$$

## B. Confusion about Work and Heat

The situation regarding  $dW(t)$  is not always clear. Kondepudi and Prigogine use  $dW(t) = PdV(t)$ , where  $P$  "...is the pressure at the moving surface," but they do not mention whether the form is applicable to all processes. Landau and Lifshitz are explicit and state that  $dW(t) = P(t)dV(t)$  for reversible and irreversible processes [34, p.45]. They require for this the *existence* of mechanical equilibrium (and so do Refs. [36, 37]) within  $\Sigma$  so that at each instant during the process  $P(t)$  must be uniform throughout the body; its equality with  $P_0$  is not required. However, they do not discuss  $dQ(t)$  when they consider  $\Sigma$  out of equilibrium with  $\tilde{\Sigma}$  [34, Sect. 20]. If we use  $dW(t) = P(t)dV(t)$  for the work *done by*  $\Sigma$ , then this will alter the heat  $dQ(t)$  *added to*  $\Sigma$  in Eq. (1). This follows immediately from the fact, not appreciated in the literature to the best of our knowledge, that  $dE(t)$  must be *invariant* to the choice of internal or external fields. Also, to the best of our knowledge, the issue of the actual forms of  $dQ(t)$  and what is the correct form of  $dW(t)$  for nonequilibrium processes

has not been settled in the literature. Indeed, Kestin [12, Sect. 5.12] clearly states that distinguishing heat and work in nonequilibrium states is not unambiguous. We will later argue otherwise in this work.

### C. Lack of Symmetry and Disconnection with the Second Law

The exchange heat and work  $d_e Q(t)$  and  $d_e W(t)$  are very different for irreversible processes, since  $d_e Q(t) \equiv T_0 d_e S(t)$  is in terms of  $d_e S(t)$ , which is not the change in a state variable, while  $d_e W(t) = P_0 dV(t)$  depends on the change in a state variable. Thus, there is an *asymmetry* between the two in the second equation in Eq. (3) in that they are not on an equal footing. However, the main disadvantage of the formulation is that it is always valid, even for a process that violates the second law by having the exchange heat flow from a colder to a hotter object. This is why we need both laws in the traditional formulation of non-equilibrium thermodynamics. We believe that an elegant formulation of a fundamental law like the first law should not only satisfy the other fundamental law, the second law but also exhibit as much symmetry as possible.

### D. Limitations

As the Gibbs fundamental relation, see Eq. (7), for the system explicitly contains the internal variable, the first law in its traditional formulation and the Gibbs fundamental relation, which codifies the second law, have different contents for irreversible processes; in particular, the latter contains more information than the former. Only for reversible processes, for which internal variables are no longer independent of the observables, the first law can be used to determine the change  $\Delta S(t) = [dE(t) + P_0 dV(t)]/T_0$  in the entropy of a body. This is not true when we deal with irreversible processes. This limits the usefulness of the first law. We now list some of the important limitations of the traditional formulation below.

- (1) The law is oblivious to the violation of the second law.
- (2) There is the above mentioned asymmetry between heat and work.

- (3) As both  $d_e Q(t)$  and  $d_e W(t)$  are determined by the medium, their knowledge does not provide us with any *direct* information about the system or its entropy change  $\Delta S(t)$  in an irreversible process. This is easily seen by considering an isolated body. As  $d_e Q(t) = d_e W(t) = 0$ , the first law has no useful content. Moreover, it cannot be used to determine  $dS(t) = d_i S(t)$  as the body changes from some state  $A'$  to a nearby state  $A$  unless both states are equilibrium states. In the latter case, one can compute  $dS(t)$  by consider some equilibrium path connecting the two states. This approach will not work if one of the two states is or both are out of equilibrium.
- (4) Work and heat cannot always be unambiguously distinguished, a point already made very strongly by Kestin [12, Sect. 5.12] and which is at the heart of the dispute discussed above.
- (5) The heat and work do not always flow through the boundary [12, footnote on p. 176].
- (6) As  $d_e S(t)$  can be determined from  $d_e Q(t)$ , the aim of any nonequilibrium thermodynamic investigation using the traditional formulation is to determine the *irreversible entropy change*  $d_i S(t)$ . For this, one needs to invoke the Gibbs fundamental relation in addition to the traditional first law; see for example de Groot and Mazur [5].
- (7) As internal variables  $\boldsymbol{\xi}(t)$  [5, 7–9, 38, 45, 47], which are very common in nonequilibrium systems such as glasses or in chemical reactions, play an important role in nonequilibrium thermodynamics, their behavior will strongly affect the dissipation within the system. Unfortunately, these variables do *not* couple to the medium [38]; hence, they do not appear in  $d_e Q(t)$  and  $d_e W(t)$ , although they control the thermodynamic relaxation and, in particular, the Gibbs fundamental relation for the system.

### III. GENERAL CONSIDERATION

As a generalization of the equilibrium concept, we use the *instantaneous values* of the state variables containing the observables  $(\mathbf{X}(t) : E(t), V(t))$  and internal variables  $(\xi(t))$  [5, 7–9] to identify the state of the body. A body can be in the same state at different times. This is important so that a system can go through a cyclic process in which the system comes back to the same initial state at a later instant. However, the entropy of

a body at some instant, besides being a function of the state variables, may also have an *explicit* dependence on time:  $S(t, E(t), V(t), \xi(t))$ . Thus, in general, the entropy will not be a state function. The first and second laws are not useful for any computation unless we can ascribe temperatures, pressures, etc. to  $\Sigma$ . This requires  $\Sigma$  and  $\tilde{\Sigma}$  to be in *internal equilibrium* [7, 8, 34] when their instantaneous entropies become *state functions*  $S(t) = S[E(t), V(t), \xi(t)]$ ,  $\tilde{S}(t) = \tilde{S}[\tilde{E}(t), \tilde{V}(t), \tilde{\xi}(t)]$  of (time-dependent) state variables. Let  $W(t) \equiv W[E(t), V(t), \xi(t)]$  and  $\tilde{W}(t) \equiv \tilde{W}[\tilde{E}(t), \tilde{V}(t), \tilde{\xi}(t)]$  denote the number of microstates consistent with the state variables for each of them. Then, as discussed in Refs. [7, 8], we have

$$S(t) = \ln W(t), \tilde{S}(t) = \ln \tilde{W}(t) \quad (5a)$$

in other words, the microstates in  $W(t)$  or in  $\tilde{W}(t)$  are *equally probable*.

The temperatures, pressures and affinities (we introduce  $\beta(t) \equiv 1/T(t)$  and  $\beta_0 \equiv 1/T_0$ ) are given by appropriate standard derivatives of the entropies:

$$\beta(t) = \partial S(t)/\partial E(t), \beta(t)P(t) = \partial S(t)/\partial V(t), \beta(t)A(t) = (\partial S(t)/\partial \xi(t); \quad (6a)$$

$$\beta_0 = \partial \tilde{S}(t)/\partial \tilde{E}(t), \beta_0 P_0 = \partial \tilde{S}(t)/\partial \tilde{V}(t), \partial \tilde{S}(t)/\partial \tilde{V}(t) = 0. \quad (6b)$$

The Gibbs fundamental relations are given by [7, 8, 34]

$$dE(t) = T(t)dS(t) - P(t)dV(t) - A(t)d\xi(t), \quad d\tilde{E}(t) = T_0 d\tilde{S}(t) - P_0 d\tilde{V}(t); \quad (7)$$

The validity of Eq. (7) requires  $\Sigma$  and  $\tilde{\Sigma}$  to be independently homogeneous [7, 8] and in internal equilibrium. We now prove the following trivial but important theorem.

**Theorem 1** *Irreversible work and irreversible heat have identical values:*

$$d_i Q(t) \equiv d_i W(t), \quad (8)$$

**Proof.** We have  $dE_0 = dV_0 = A_0 = 0$  for  $\Sigma_0$ . The application of the first law for  $\Sigma_0$  using generalized heat and work, see Eq. (2), gives

$$dE_0 = dQ_0(t) - dW_0(t) \equiv d_i Q_0(t) - d_i W_0(t) = 0; \quad (9)$$

there is no exchange heat and no exchange work for  $\Sigma_0$ . As the irreversibility is only associated with the system  $\Sigma$ , we have  $d_i Q(t) = d_i Q_0(t)$  and  $d_i W(t) = d_i W_0(t)$ . The desired equality in Eq. (8) now follows from Eq. (9). ■

The statistical demonstration of the identity in Eq. (8) is given in Theorem 6. It is now easy to show that heat and work can also be used in the first law for the system ( $dE(t) = dQ(t) - dW(t)$ ), since  $dQ(t) - dW(t) \equiv d_e Q(t) - d_e W(t)$ . For the medium, it also holds ( $d\tilde{E}(t) = d\tilde{Q}(t) - d\tilde{W}(t)$ ) as  $d_i \tilde{Q}(t) = d_i \tilde{W}(t) = 0$ . Thus, we can express the first law for any body by also using generalized heat and work; see Eq. (1).

It was established in Ref. [7] that

$$dQ(t) = T(t)dS(t). \quad (10)$$

It is a generalization of  $d_e Q(t) \equiv T_0 d_e S(t)$  to  $dQ(t)$ ; the latter denotes the *heat added to the system* either through exchange with its exterior ( $d_e Q(t)$ ) or by dissipative internal forces within ( $d_i Q(t)$ ). Similarly,

$$dW(t) = d_e W(t) + d_i W(t) = P(t)dV(t) + A(t)d\xi(t) \quad (11)$$

is the generalization of work done by the system: it includes the work done on its exterior ( $d_e W(t)$ ) and the (internal) work done by dissipative internal forces ( $d_i W(t)$ ).

To appreciate the importance of the new definition of heat and work, let us for the moment assume that there is no internal variable and that  $P(t) > P_0$ . The irreversible work  $d_i W_0(t)$  done in  $\Sigma_0$  by the pressure difference  $\Delta P(t) = P(t) - P_0 > 0$  is

$$dW_0(t) \equiv d_i W_0(t) = \Delta P(t)dV(t) > 0,$$

since  $dV(t) > 0$ , and appears as the irreversible work within the system and results in raising the kinetic energy  $dK_S$  of the center-of-mass of the surface separating  $\Sigma$  and  $\tilde{\Sigma}$  and overcoming work  $dW_{\text{fr}}(t)$  done by all sorts of viscous or frictional drag. Thus,

$$d_i W_0(t) \equiv dK_S + dW_{\text{fr}}(t). \quad (12)$$

Because of the stochasticity associated with any statistical system, both energies on the right side dissipate among the particles so as to increase the entropy and appear in the form of heat ( $d_i Q_0(t) = d_i Q(t) > 0$ ) within the isolated system [39]. Thus, when there are irreversible processes going on, it is natural to generalize heat from  $d_e Q(t)$  in Eq. (3) to include  $d_i Q(t) = d_i Q_0(t)$  and identify  $dQ(t)$  as the *heat added to the system*. Similarly, we need to generalize work from  $d_e W(t) = P_0 dV(t)$  to  $dW(t) = P(t)dV(t)$  and identify it as *work done by the system*. In the presence of the internal variable, there is an additional contribution ( $A(t) - A_0$ ) $d\xi(t) = A(t)d\xi(t) > 0$  to  $dW(t)$ . This does not change the conclusions above.

We finally conclude that

$$dE(t) = d_e Q(t) - d_e W(t) \equiv dQ(t) - dW(t) \quad (13)$$

which demonstrates that both formulations are *valid* for the first law. However, the most important result is given by Eq. (10). We also see that  $d_i Q(t) \neq T_0 d_i S(t)$ ,  $d_i Q(t) \neq T(t) d_i S(t)$ , even though  $d_e Q(t) = T_0 d_e S(t)$ ; see Eq. (16).

The equality in Eq. (8) can also be obtained by the use of the Gibbs fundamental relation. We follow the approach initiated in Ref. [8], and rewrite  $dE(t)$  by explicitly exhibiting the thermodynamic forces as follows:

$$dE(t) = T_0 d_e S(t) - P_0 dV(t) + T_0 d_i S(t) + [T(t) - T_0] dS(t) + [P_0 - P(t)] dV(t) - A(t) d\xi(t)$$

to conclude that

$$T_0 d_i S(t) + [T(t) - T_0] dS(t) + [P_0 - P(t)] dV(t) - A(t) d\xi(t) = 0. \quad (14)$$

For this to be valid, each of the last three terms must be non-positive:

$$[T_0 - T(t)] dS(t) \geq 0, [P(t) - P_0] dV(t) \geq 0, A(t) d\xi(t) \geq 0, \quad (15)$$

to ensure that  $d_i S(t) \geq 0$ . The factors  $T_0 - T(t)$ ,  $P(t) - P_0$  and  $A(t)$  in front of the extensive state variables are the corresponding thermodynamic forces that act to bring the system to equilibrium. In the process, each force generates its own irreversible entropy generation [8]. The equalities occur when thermodynamic forces vanish.

It is useful to acknowledge at this point that there are no thermodynamic forces in the medium. To see this, we consider Eq. (7) for  $d\tilde{E}(t)$ , in which both terms contain the constant fields  $T_0$  and  $P_0$  of the medium, clearly showing that the thermodynamic forces are zero. This means that there cannot be any irreversible entropy generation within the medium; they only appear within the system, as we have said earlier.

We now recognize that

$$d_i Q(t) = T_0 d_i S(t) + [T(t) - T_0] dS(t), \quad (16a)$$

$$= T(t) d_i S(t) + [T(t) - T_0] d_e S(t) \quad (16b)$$

and

$$d_i W(t) = [P(t) - P_0] dV(t) + A(t) d\xi(t). \quad (17)$$

Their equality merely reflects the fact that in the partition  $dE(t) = d_e E(t) + d_i E(t)$ ,  $d_i E(t) \equiv 0$ . We also note that while each term in  $d_i W(t)$  is non-negative, this is not so for  $d_i Q(t)$  in which the first term is non-negative, but the second term in Eq. (16) is non-positive. This not only means that *the physics of  $d_i Q(t)$  and  $d_i S(t)$  is very different* but also that

$$d_i Q(t) \leq T_0 d_i S(t), dQ(t) \leq T_0 dS(t); \quad (18)$$

the equalities occur only for isothermal ( $T = T_0$ ) or adiabatic ( $dS = 0$ ) processes. Even though  $dQ(t) = T(t)dS(t)$  for a system *not* in equilibrium with the medium, we have  $d_e Q(t) \neq T(t)d_e S(t)$ ,  $d_i Q(t) \neq T(t)d_i S(t)$ . *It should become evident by now that it would be incorrect to use  $dS(t) = d_e Q(t)/T_0 + d_i S(t)$  to conclude  $d_i Q(t) = T_0 d_i S(t)$ .*

In the general case, the first law can be written as

$$dE(t) = \frac{\partial E(t)}{\partial \bar{\mathbf{Z}}(t)} \cdot d\bar{\mathbf{Z}}(t),$$

where  $\bar{\mathbf{Z}}(t)$  contains  $S(t)$  and the set  $\mathbf{Z}_E(t)$  consisting of all state variables except  $E(t)$ . We clearly see that each term in the scalar product has the same mathematical form, ensuring that *all terms are on an equal footing*. It is this symmetry that was absent in the traditional formulation, but is present in the new formulation of the first law. As this is also the general form of the Gibbs fundamental relation, *the two laws have reduced to a single law*, as we have claimed. Therefore, our formulation of the first law will always remain consistent with the second law.

#### IV. GENERALIZED WORK AND THE SECOND LAW

Let us follow the consequences of this particular generalization a bit further by again restricting to no internal variable for simplicity, and prove that only  $dW(t) = P(t)dV(t)$ ,  $d\widetilde{W}(t) = P_0 d\widetilde{V}(t)$  using the internal pressures of the bodies is consistent with the second law, and not  $dW(t) = P_0 dV(t)$ ,  $d\widetilde{W}(t) = P(t)d\widetilde{V}(t)$  which use the pressures external to the bodies. These choices for work are *symmetric* as opposed to the traditional formulation in Sec. II in which there is no symmetry between  $d_e W(t)$  and  $d_e \widetilde{W}(t)$ .

We take  $P(t) > P_0$  and consider the choice  $dW(t) = P(t)dV(t)$  etc. We obtain  $dW(t) + d\widetilde{W}(t) = P(t)dV(t) + P_0 d\widetilde{V}(t)$  valid for any arbitrary  $dV(t) = -d\widetilde{V}(t)$  so that

$$d_i W(t) = [P(t) - P_0] dV(t) > 0, \quad (19)$$



which is consistent with the second law and proves the above assertion, once we recognize that  $dV(t) > 0$ . The second choice will result in the violation the second law, since  $dW_i(t) = (P_0 - P(t))dV(t) < 0$ , a physical impossibility. Thus, we must write the first law for the system and the medium, respectively, as  $dE(t) = dQ(t) - P(t)dV(t)$ ,  $d\tilde{E}(t) = d\tilde{Q}(t) - P_0d\tilde{V}(t)$ . The above discussion is easily extended to include internal variables without affecting the above conclusion.

The above demonstration establishes that the work done by a body is given by Eq. (11) in *all* cases contrary to the traditional formulation, see Eq. (3), in which it is given by  $P_0dV(t)$ . The generalized formulation brings out the another symmetry: under the interchange system $\longleftrightarrow$ medium, work and heat for any body always uses its own internal fields. This symmetry is absent in the traditional formulation. The new symmetry will prove very useful when the medium is not extensively large compared to the system or when we need to consider mixing of gases, free expansion, etc. where there is no clear separation between different parts of an isolated system into a system and a medium.

## V. STATISTICAL DEFINITION OF WORK AND HEAT

### A. System

#### 1. System not in Internal Equilibrium

Before proceeding further, let us see how the generalized heat and work could be understood from a statistical point of view. We consider two possible neighboring nonequilibrium states A and A' at different times  $t$  and  $t' < t$ , respectively, so that the differences in their state variables  $dE(t) \equiv E(t) - E'(t')$ ,  $dV(t) \equiv V(t) - V'(t')$ ,  $d\xi(t) \equiv \xi(t) - \xi'(t')$  and the difference  $dS(t) \equiv S(t) - S'(t')$  in their entropies are infinitesimal. We use the index  $i$  to label the microstates of the system and let  $p_i(t), p'_i(t')$  their probabilities in A and A', respectively. These probabilities are functions of the state variables (including the number of particles, but that remains constant) and may also have an explicit time dependence. Thus, the discussion here does not require the system to be in internal equilibrium. Obviously [48]

$$\sum_i p_i(t) = \sum_i p'_i(t) \equiv 1. \quad (20)$$

We will see below, see Theorem 6, that the probability conservation is behind the statistical demonstration of the identity in Eq. (8). The energy  $E_i$  of the  $i$ th microstate, on the other hand, depends on  $V(t)$  and  $\xi(t)$  [in general,  $E_i$  will depend on the set  $\mathbf{Z}_E(t)$ ], but will have no explicit  $t$ -dependence. The entropy  $S$  and the energy  $E$  are given by the following averages

$$S(t) \equiv \sum_i p_i(t) \eta_i(t), \quad E(t) \equiv \sum_i p_i(t) E_i(t), \quad (21)$$

where

$$\eta_i \equiv -\ln p_i(t) \quad (22)$$

is the uncertainty of Shanon or the negative of the index of probability of Gibbs [9, 39] and  $E_i(t)$  is the energy of the  $i$ th microstate. (We will avoid the use of microstate "entropy," to refer to  $\eta_i$ , which has become common in the literature these days.) The entropy expression is due to Gibbs [35]. We have exhibited a time-dependence in  $E_i(t)$  to reflect the fact that this energy can change as  $V(t)$  and  $\xi(t)$  change during the transition  $A' \rightarrow A$ . The microstate probability will also change in time. In particular, *a microstate may disappear or a new microstate may emerge in time*. This is most easily seen by recognizing, see Eq. (5), that the entropy is determined by  $W(t)$ . As entropy changes,  $W(t)$  must change so that either some previous microstates disappear or some new microstate emerge. All this will become clear below in Sec. V G where we discuss a simple example of an ideal gas. We now prove

**Theorem 2**  *$E(t)$  is a function of  $V(t), \xi(t)$  and  $S(t)$ , even though  $E_i[V(t), \xi(t)]$  are functions of  $V(t)$  and  $\xi(t)$  only.*

**Proof.** We consider the differential

$$dE(t) \equiv \sum_i E_i(t) dp_i(t) + \sum_i p_i(t) dE_i(t).$$

As  $p_i(t)$  are unchanged in the first sum, this sum is evaluated at *constant entropy*. Thus, this contribution is isentropic which we denote by  $dE|_S$ . The microstate energies  $E_i$  are unchanged in the second sum so this contribution refers to an isometric process at fixed  $V(t)$  and  $\xi(t)$  and we denote the contribution by  $dE|_{V,\xi}$ . Thus,

$$dE \equiv dE|_{V,\xi} + dE|_S. \quad (23)$$

This proves that  $E(t)$  is a function of  $S(t), V(t)$  and  $\xi(t)$ . ■

In general,  $E(t)$  is a function of  $S(t)$  and the set  $\mathbf{Z}_E(t)$ . We introduce a special process, to be called an *isometric* process, which is a process at constant  $\mathbf{Z}_E(t)$  and is a generalization of an *isochoric* process. In this process, the work done by each mechanical variables in  $\mathbf{Z}_E(t)$  remains zero. We now prove the following theorem that establishes the physical significance of the two contributions.

**Theorem 3** *The isentropic contribution represents the generalized work  $dW(t)$  and the isometric contribution represents the generalized heat  $dQ(t)$ .*

**Proof.** We follow Landau and Lifshitz [34] and rewrite the second term in Eq. (23) as

$$dE|_S \equiv \sum_i p_i(t) \frac{\partial E_i}{\partial V} dV(t) + \sum_i p_i(t) \frac{\partial E_i}{\partial \xi} d\xi(t) = -\sum_i p_i(t) P_i(t) dV(t) - \sum_i p_i(t) A_i(t) d\xi(t)$$

where we have introduced  $P_i(t) \equiv -\partial E_i(t)/\partial V(t)$  as the pressure produced by the  $i$ th microstate of the system [49, p. 67] on its boundary. This pressure corresponds to a force pointing *away* from the system. Similarly,  $A_i(t) \equiv -\partial E_i(t)/\partial \xi(t)$  as the affinity of the  $i$ th microstate. We assume that the changes  $dV(t)$  and  $d\xi(t)$  are the same for all microstates so that they can be taken out of the summations. In terms of

$$P(t) = \sum_i p_i(t) P_i(t), A(t) = \sum_i p_i(t) A_i(t), \quad (24)$$

respectively, which define the instantaneous *average pressure*  $P(t)$  and *affinity*  $A(t)$  of the system, respectively, we can relate  $dE|_S$  with  $dW(t)$  and nit with  $d_e W(t)$ :

$$dW(t) \equiv -dE|_S = P(t) dV(t) + A(t) d\xi(t). \quad (25)$$

This identification then also proves that the heat in the first law must be properly identified with  $dQ$  and not with  $d_e Q$ . Accordingly,

$$dQ \equiv dE|_{V,\xi} \equiv \sum_i E_i dp_i, \quad (26)$$

i.e.,  $dQ$  for irreversible processes is *the isometric change in the energy*. ■

We should point out that by assuming  $dV(t)$  and  $d\xi(t)$  above to be the same for all microstates, the statistical nature of  $dE|_S$  is reflected in the statistical nature of  $P(t)$  and  $A(t)$ , the internal fields of the system. Thus, the internal fields are fluctuating quantities from microstate to microstate when  $dV(t)$  and  $d\xi(t)$  are not treated statistically.

In general,  $dE|_S$  will be a sum of various works  $dW_Z(t) = -(\partial E/\partial Z)_{S, \mathbf{Z}'_E} dZ$ , with  $\mathbf{Z}'_E(t)$  consisting of all state variables in  $\mathbf{Z}_E(t)$  except  $Z(t)$  used in the derivative:

$$dE|_S \equiv -dW(t) = - \sum_{Z \in \mathbf{Z}_E(t)} dW_Z(t). \quad (27)$$

This is again consistent with the previously mentioned symmetry in the new formulation.

The above discussion proves that the definition of heat and work does not require the establishment of the internal equilibrium within the system. It is useful to compare the above approach with the traditional formulation of the first law in terms of  $d_e Q(t)$  and  $d_e W(t)$ : *both formulations are valid in all cases*. It should be mentioned that the above identification is well known in equilibrium statistical mechanics, but its extension to irreversible processes and our interpretation is, to the best of our knowledge, is novel.

We now prove a trivial but conceptually an important theorem.

**Theorem 4** *Heat and work in the traditional formulation of the first law do not have a clear division as in Eq. (23).*

**Proof.** To prove the theorem, we focus on  $d_e W(t) = P_0 dV(t)$  and recognize that  $P_0$  is a constant. Hence, the statistical nature of  $d_e W(t)$  must be contained in  $dV(t)$ . As  $V(t) = \sum_i p_i V_i$ , we have

$$d_e W(t) = P_0 (\sum_i p_i dV_i + \sum_i V_i dp_i).$$

We observe that  $d_e W(t)$  contains not only an isentropic contribution, the first sum on the right, but also contains a contribution containing  $dp_i$ . Thus, the clear separation between heat and work, as appears in Theorem 2, is not present in the traditional formulation of the first law. ■

## 2. System in Internal Equilibrium

It should be clear from the existence of non-zero thermodynamic forces for irreversibility, that  $P(t) \neq P_0 = \left( \partial \tilde{E} / \partial V \right)_{\tilde{S}, \tilde{\xi}}$  except when a mechanical equilibrium exists. While the instantaneous average pressure is defined under all circumstances, it can only be identified with the thermodynamic definition of the instantaneous pressure

$$P(t) = -(\partial E / \partial V)_{S, \xi} \quad (28)$$

when the system is in internal equilibrium. Similarly, the instantaneous average affinity  $A(t)$  of the state has nothing to do with the affinity of the medium ( $A_0 = 0$ ), and can only be identified with its thermodynamic definition  $A(t) = -(\partial E/\partial \xi)_{S,V}$  when the system is in internal equilibrium. To proceed further, we need to impose the condition of internal equilibrium, so that  $p_i$  has no explicit time-dependence. In this case, not only the instantaneous pressure satisfies Eq. (28), but we also have, following Eq. (26),

$$dQ(t)/dS(t) = (\partial E/\partial S)_{V,\xi} = T(t), \quad (29)$$

which is a statistical proof of the thermodynamic identity in Eq. (10) relating  $dQ(t)$  and  $dS(t)$ . We also note that the ratio  $dQ(t)/dS(t)$  is related to a field variable of a (macro)state, the instantaneous temperature of the system, while in the conventional approach, the ratio  $d_e Q(t)/d_e S(t) = T_0$  does not give a field variable of the state.

It is clear from the above discussion that it is heat and not work that causes  $p_i(t)$ , and therefore the entropy, to change without changing  $E_i$ . This is the essence of the common wisdom that heat is *random motion*. But we now have a mathematical definition: heat is the isometric part of  $dE(t)$  that is directly related to the change in the entropy through changes in  $p_i(t)$ . Work is that part of the energy change caused by isentropic variations in the "mechanical" state variables  $\mathbf{Z}_E(t)$ . Thus, work causes  $E_i$  to change without changing  $p_i(t)$ . This is true no matter how far the system is from equilibrium. Thus, our formulation of the first law and the identification of the two terms is the most general one, and applicable in all cases. *The relationship between heat and entropy becomes simple only when the system is also in internal equilibrium in which case  $T(t)$  has a thermodynamic significance; see Eq. (6a) and we have the thermodynamic identity in Eq. (10) relating  $dQ(t)$  and  $dS(t)$ .*

## B. Microstate probabilities

In internal equilibrium, the entropy must be at its maximum at fixed  $E(t) = \sum_i E_i p_i$ ,  $V(t) = \sum_i V_i p_i$  and  $\xi(t) = \sum_i \xi_i p_i$ , and is obtained by varying  $p_i$  without changing the microstates, i.e.  $E_i$ ,  $V_i$  and  $\xi_i$ . This variation has nothing to do with  $dp_i$  in a physical process. Using the Lagrange multiplier technique, it is easy to show that the condition for this in terms of four Lagrange multipliers whose definitions are obvious is

$$\eta_i = \lambda_1 + \lambda_2 E_i + \lambda_3 V_i + \lambda_4 \xi_i, \quad (30)$$

from which follows  $S = \lambda_1 + \lambda_2 E + \lambda_3 V + \lambda_4 \xi$ . It is now easy to identify  $\lambda_2 = \beta$ ,  $\lambda_3 = \beta P$  and  $\lambda_4 = \beta A$  so we finally have

$$p_i(t) = \exp[\beta(t)(\widehat{G}(t) - E_i - P(t)V_i - A(t)\xi_i)], \quad (31)$$

where  $\lambda_1 = \beta(t)\widehat{G}(t)$  with  $\widehat{G}(t)$  defined by

$$\exp(-\beta(t)\widehat{G}(t)) \equiv \sum_i \exp[-\beta(t)(E_i + P(t)V_i + A(t)\xi_i)].$$

The quantity  $\widehat{G}(t)$  would represent the free energy of the system, had it been in a medium  $\widetilde{\Sigma}(T, P, A)$ . However, as the system is in a medium  $\widetilde{\Sigma}(T_0, P_0, A_0 = 0)$ ,  $\widehat{G}(t)$  does not represent the free energy in this case; the correct free energy of the system is the Gibbs free energy  $G(T_0, P_0) = E(t) - T_0 S(t) + P_0 V(t)$ ; see Ref. [8] for more details. The microstate probability  $p_i(t)$  in Eq. (31) clearly shows the effect of irreversibility and is very different from its equilibrium analog  $p_{i,\text{eq}}$

$$p_{i,\text{eq}} = \exp[\beta_0(G(T_0, P_0) - E_i - P_0 V_i)].$$

We now provide another demonstration that the two terms in Eq. (23) are identical to the generalized heat and work in the following theorem.

**Theorem 5** *The heat and work in Eqs. (10) and (11), and (23) are the same.*

**Proof.** We first note the identity

$$\sum_i (\eta_i - \beta(t)E_i) dp_i = 0,$$

which is nothing but the identity  $dQ(t) = T(t)dS(t)$ . Using this identity, we obtain another identity that follows from Eq. (30)

$$P(t)\sum_i V_i dp_i(t) + A(t)\sum_i \xi_i dp_i(t) = 0, \quad (32)$$

where being related to the Lagrange multipliers,  $P(t)$ ,  $A(t)$ , etc. must be treated as parameters. We now rewrite  $dV(t) = \sum_i V_i(t) dp_i(t) + \sum_i p_i(t) dV_i(t)$  and  $d\xi(t) = \sum_i \xi_i(t) dp_i(t) + \sum_i p_i(t) d\xi_i(t)$  in  $dW(t) = P(t)dV(t) + A(t)d\xi(t)$  and use the above identity in Eq. (32) to establish that the work in Eqs. (11) reduces to the isentropic form  $dW(t) = P(t)\sum_i p_i(t) dV_i + A(t)\sum_i p_i(t) d\xi_i(t)$ . As  $P(t)$  and  $A(t)$  are parameters, the statistical nature of  $dW(t)$  appears

in  $dV(t)$  and  $d\xi(t)$ . As the work expressions are identical, the demonstration also proves that the thermodynamic parameters in Eq. (31) and the statistical fields in Eq. (24) are the same. ■

This proves the two formulations of work to be identical. Apart from providing a check for the internal consistency in our approach, this also proves that the first term in Eq. (23) is identical to the heat in Eq. (10). At equilibrium,  $A(t) \rightarrow A_0 = 0$  and the second term in Eq. (32) vanishes. As  $P(t) \rightarrow P_0$  at equilibrium, we conclude that  $d_e W(t) = P_0 \sum_i p_i dV_i$ , see Theorem 4, which makes  $d_e W(t)$  purely isentropic, as expected.

Let us compute the generalized pressure work  $W(t)$  done by the system over some time interval  $t$  at *fixed*  $p_i(t)$  as  $V(t)$  [ $\dot{V}(t) \equiv dV(t)/dt$ ] changes from its initial value. It is given by the integral

$$W_V(t) = \sum_i p_i(t) \int_0^t p_i(t) P_i(t) \dot{V}(t) dt \equiv \int_0^t P(t) \dot{V}(t) dt \quad (33)$$

and differs from the negative of the work  $\widetilde{W}(t) = P_0 \Delta \widetilde{V}(t)$  (obtained by replacing all the quantities in Eq. (33) by their medium analogs) done by the medium on the system by the dissipative contribution. This result should be contrasted with the result obtained by others [42]. They become identical if and only if the average pressure  $P(t)$  is *identical* with  $P_0$ .

### C. Medium

The above discussion can be easily extended to the medium (the suffix  $\tilde{\alpha}$  denotes its microstates) with the following results

$$\begin{aligned} d\widetilde{W}(t) &= -d\widetilde{E}\Big|_{\widetilde{S}} \equiv -\sum_{\tilde{\alpha}} \tilde{p}_{\tilde{\alpha}} \frac{\partial \widetilde{E}_{\tilde{\alpha}}}{\partial \widetilde{V}} d\widetilde{V} = P_0 d\widetilde{V}, \\ d\widetilde{Q}(t) &= d\widetilde{E}\Big|_{\widetilde{V}} \equiv \sum_{\tilde{\alpha}} \widetilde{E}_{\tilde{\alpha}} d\tilde{p}_{\tilde{\alpha}} \equiv d\widetilde{Q} \equiv -d_e Q, \end{aligned}$$

where all the quantities refer to the medium, except  $d_e Q$ , and have their standard meaning. The analog of Eq. (29) is

$$d\widetilde{Q}/d\widetilde{S} = \left( \partial \widetilde{E} / \partial \widetilde{S} \right)_{\widetilde{V}, \xi} = T_0, \quad (34)$$

as expected. We clearly see that

$$dW + d\widetilde{W} \neq 0$$

such as when mechanical equilibrium is not present. In this case, we also have

$$dQ + d\widetilde{Q} \neq 0.$$

## D. Irreversible Work and Heat

We can now identify  $d_i W(t)$  and  $d_i Q(t)$  :

$$\begin{aligned} d_i W(t) &\equiv -(dE|_S + d\tilde{E}|_{\tilde{S}}) \\ d_i Q(t) &\equiv (dE|_{V,\xi} + d\tilde{E}|_{\tilde{V},\tilde{\xi}}), \end{aligned}$$

with  $d_i Q(t) \equiv d_i W(t)$  from Theorem 1. Because of the equality, we only need to compute one of them, which we take to be  $d_i W(t)$ , merely because it only involves adiabatic quantities. However, the computation of irreversible work requires considering both the system and the (working part of the) medium, which makes their computation quite unfeasible in many situations because of the very large size of the medium, unless the equations of state of the medium are known. On the other hand, the determination of  $dW(t)$  and  $dQ(t)$  is a much easier task computationally as we only deal with the system, a point made several times in the literature; see, for example, Jarzynski [17].

## E. External and Internal Variations of $dp_i(t)$

Let us introduce the natural partition as in Eq. (2) for  $dp_i$ :

$$dp_i(t) = d_e p_i(t) + d_i p_i(t);$$

$d_e p_i(t)$  is the change due to exchanges with the medium and  $d_i p_i(t)$  the change due to internal dissipation  $d_i Q$ . Then we have

$$d_e Q(t) \equiv \sum_i E_i d_e p_i(t), \quad d_i Q(t) \equiv \sum_i E_i d_i p_i(t). \quad (35)$$

We similarly have

$$d_e S(t) \equiv \sum_i \eta_i d_e p_i(t), \quad d_i S(t) \equiv \sum_i \eta_i d_i p_i(t). \quad (36)$$

We can recast Eq. (16)

$$\sum_i (E_i - T_0 \eta_i) d_i p_i = (T(t) - T_0) \sum_i \eta_i d_i p_i$$

that acts as a constraint on possible variations  $d_i p_i$ . The relation  $d_e Q(t) = T_0 d_e S(t)$  can be expressed in terms of  $d_e p_i(t)$

$$\sum_i (\eta_i - \beta_0 E_i) d_e p_i = 0.$$

We now prove the following theorem.



**Theorem 6** *The identity in Eq. (8) is a consequence of the vanishing of average change in microstate uncertainty*

$$\sum_i p_i d\eta_i = \sum_i dp_i = 0,$$

*which is nothing but the conservation of probability.*

**Proof.** We express Eq. (8) in terms of microstate probabilities and use Eq. (32) to obtain

$$\sum_i E_i d_i p_i(t) = P(t) \sum_i p_i(t) dV_i + A(t) \sum_i p_i(t) d\xi_i(t) - P_0 dV.$$

We eliminate the last term using the traditional formulation of the first law to obtain

$$\sum_i p_i(t) [dE_i(t) + P(t) dV_i + A(t) d\xi_i(t)] = 0.$$

In view of Eq. (30), this is nothing but  $\sum_i p_i d\eta_i = 0$ . This proves the theorem. ■

## F. The Adiabatic Theorem

We now have a clear statement of the generalization of the adiabatic theorem [34] for nonequilibrium processes. *An adiabatic nonequilibrium process is an isentropic process.* Such a process also includes the stationary limit, i.e. the steady state of a non-equilibrium process. However, the extension goes beyond the conventional notion of an adiabatic process commonly dealt with in equilibrium statistical mechanics according to which an adiabatic process is one for which  $d_i S = 0$ , and represents a reversible process in a thermally isolated system so that  $d_e Q(t) = 0$ . One can also have  $dS = 0$  in an irreversible process during which

$$d_i S(t) = -d_e S(t) > 0; \tag{37}$$

as usual, Eq. (8) always remains satisfied. If the system remains in internal equilibrium, which may not hold for a stationary state, then we must also have

$$d_i Q(t) = -d_e Q(t) = T_0 d_i S(t) > 0. \tag{38}$$

In the following, we will not consider a stationary nonequilibrium state, a case that would be taken up elsewhere.

**Theorem 7** *In an adiabatic process, the sets of microstates and of their probabilities  $p_i$  do not change, but  $d_e p_i = -d_i p_i \neq 0$  for all  $i$ .*

**Proof.** In terms  $d_e p_i$  and  $d_i p_i$ , Eqs. (37) and (38) become

$$\sum_i \eta_i d_i p_i = - \sum_i \eta_i d_e p_i, \quad (39a)$$

$$\sum_i E_i d_i p_i = - \sum_i E_i d_e p_i. \quad (39b)$$

Recognizing that there is only work in the defining relation in Eq.(23), which requires  $p_i$  not to change, we conclude that

$$dp_i = 0 \quad \text{for } \forall i$$

in an adiabatic process. As  $d_i S(t)$  does not vanish in an irreversible process,  $d_i p_i(t)$  cannot vanish. Accordingly,  $d_e p_i = -d_i p_i \neq 0$  for an irreversible adiabatic process. As  $p_i$ 's do not change, no microstate can appear or disappear. This proves the theorem. ■

### G. Ideal Gas: An Illustrative Example

Consider, as an example, an ideal gas in a cuboid with its axis along the  $x$ -axis. Its length  $a(t)$  along the  $x$ -axis is controlled by a frictionless piston at one end. All other walls are assumed rigid. Let the dimensions  $b$  and  $c$ , respectively, along the  $y$ - and  $z$ - axes remain constant. As the particles are ideal, we can focus on single particle energy levels given by

$$E_{\mathbf{n}} = \frac{\hbar^2 \pi^2}{2m} \left( \frac{n_1^2}{a^2(t)} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2} \right),$$

with the corresponding wavefunction given by

$$\phi_{\mathbf{n}}(\mathbf{r}(t)) = \sqrt{\frac{8}{a(t)bc}} \sin\left(\frac{n_1}{\pi a(t)}x\right) \sin\left(\frac{n_2}{\pi b}y\right) \sin\left(\frac{n_3}{\pi c}z\right),$$

which form the normalized complete basis set. Let  $p_{\mathbf{n}}(t)$  denote the probability of having gas particles in a given eigenstate  $\mathbf{n}$ . Then the energy per particle of the gas is given by

$$E(t) = \sum_{\mathbf{n}} p_{\mathbf{n}}(t) E_{\mathbf{n}}(t),$$

and the pressure on the moving piston is given by

$$P(t) = \frac{1}{bc} \left( -\frac{dE}{da(t)} \right) = \frac{\hbar^2 \pi^2}{mV(t)} \sum_{\mathbf{n}} p_{\mathbf{n}}(t) \frac{n_1^2}{a^2(t)} = \frac{2}{V(t)} (E(t) - E_0),$$

where

$$E_0 = \sum_{\mathbf{n}} p_{\mathbf{n}}(t) \frac{\hbar^2 \pi^2}{2m} \left( \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2} \right).$$

The probabilities and the energy eigenvalues change in time as a function of  $a(t)$ . The change in the energy  $E(t)$  comes from changes in  $p_{\mathbf{n}}(t)$  and from the variations in  $a(t)$ . The two contributions determine heat and work, respectively.

If the system of ideal gas is isolated, its energy, volume and the number of particles remain constant. If the gas is originally not in equilibrium, it will eventually reach equilibrium in which its entropy must increase. This requires the introduction of some internal variables even in this system whose variation will give rise to entropy generation by causing internal variations  $d_i p_{\mathbf{n}}(t)$  in  $p_{\mathbf{n}}(t)$ . Here, we will assume a single internal variable  $\xi(t)$ . Its real nature is not relevant for our discussion. What is relevant is that the variation in  $\xi(t)$  is accompanied by changes  $d_i p_{\mathbf{n}}(t)$  occurring within the isolated system. According to our identification of heat with changes in  $p_{\mathbf{n}}(t)$ , these variations must be associated with heat, which in this case will be associated with irreversible heat  $d_i Q(t)$ .

### 1. Isothermal Expansion

Let us first consider an isothermal expansion of this gas so that the temperature of the gas remains constant and equal to that of the medium  $T_0$ . During expansion, energy is pumped into the gas isothermally from outside so that not only  $E(t)$  remains constant, but also keeps  $P(t)V(t)$ . The pumping of energy will result in the change  $d_e p_{\mathbf{n}}(t)$ . This will determine  $d_e Q(t) = T_0 d_e S(t)$ . In addition, particles may undergo transitions among various energy levels, as discussed above, without any external energy input, which will determine the change  $d_i p_{\mathbf{n}}(t)$ . This will determine  $d_i Q(t) = T_0 d_i S(t)$ , and consequently  $d_i W(t)$ . Thus,

$$[P(t) - P_0]dV(t) + A(t)d\xi(t) = T_0 dS(t) - d_e Q(t),$$

which allows us to determine the irreversible work in terms of measurable quantities. Such a calculation will not be possible in the traditional formulation of the first law.

### 2. Adiabatic Expansion

In a nonequilibrium adiabatic process, we have  $d_i W(t) = -d_e Q(t)$  so the heat exchange  $|d_e Q(t)| = T_0 |d_e S(t)|$  is converted into the irreversible work in this process. We can use this to determine the work  $d_i W_{\xi}(t)$  due to the internal variable

$$A(t)d\xi(t) = -d_e Q(t) - (P(t) - P_0)dV > 0.$$

The identification  $d_i W(t) = -d_e Q(t)$  and the calculation of  $A(t)d\xi(t)$  cannot be done in the traditional formulation of the first law.

## VI. CLAUSIUS EQUALITY

It follows from Eq. (10) that  $dQ(t)/T(t)$  is nothing but the *exact differential*  $dS(t)$  so that

$$\oint dQ(t)/T(t) \equiv 0 \text{ for any cyclic process.} \quad (40)$$

We will call it the *Clausius equality*. The equality should not be interpreted as the absence of irreversibility; see Eq. (4). It is only because of the use of the generalized heat  $dQ(t)$  in place of  $d_e Q(t)$  that the Clausius inequality has become an equality. Using  $d_i S(t) \equiv dS(t) - d_e S(t)$ , we obtain the original Clausius inequality for a cyclic process taking time  $\tau$ :

$$N(t, \tau) \equiv \oint d_i S(t) = -\oint d_e Q(t)/T_0 \geq 0, \quad (41)$$

which is the second law for a cyclic process and represents the irreversible entropy generated in a cycle; see Eq. (4). The quantity  $N(t)$  is the *uncompensated transformation* of Clausius [6] that, as we have just discovered, is directly related to  $d_i S(t)$  [50]; in contrast,  $N_0(t, \tau)$

$$N_0(t, \tau) \equiv \oint d_i Q(t)/T(t) \quad (42)$$

is determined by the *uncompensated heat*  $d_i Q(t)$  and represents a different quantity. In terms of the two heats, we have

$$\oint d_i Q(t)/T(t) = -\oint d_e Q(t)/T(t) \geq 0, \quad (43)$$

which results in a new Clausius inequality

$$\oint d_e Q(t)/T(t) \leq 0; \quad (44)$$

compare with the original Clausius inequality in Eq. (4). The contribution  $N_0(t)$  in Eq. (43) can be thought of as a new uncompensated transformation, different from  $N(t)$  [6]. Our formulation has allowed us to identify the two transformations

$$N(t, \tau) \equiv \oint d_i S(t) \equiv \oint d_i Q(t)/T_0 - \oint T(t)dS(t)/T_0, \quad N_0(t, \tau) \equiv \oint d_i Q(t)/T(t) \equiv \oint d_i W(t)/T(t),$$

which provides a way of computing them using nonequilibrium equations of state of  $\Sigma$  and  $\tilde{\Sigma}$ .

Other quantities also appear as equalities. Let us consider work, which appears as  $dW(t) = -[dE(t) - T(t)dS(t)]$ . For a not too small a change, we have

$$\Delta W(t) = -\Delta \hat{F}(t) \equiv \Delta [E(t) - T(t)S(t)]. \quad (45)$$

The quantity  $\hat{F}(t)$  in the brackets should not be confused with the Helmholtz free energy  $F(t) \equiv E(t) - T_0 S(t)$ . The above equalities should be contrasted with the traditional inequalities  $d_e W(t) \leq -dF(t)$  or  $\Delta_e W(t) \leq -\Delta F(t)$ .

## VII. APPLICATIONS

We now consider two simple applications of the new approach.

### A. Free Expansion

Consider the example of free expansion in a set up in which gas in one chamber is separated from another empty chamber of identical volume  $V^0$  by a partition; the latter is held stationary by some mechanism. Both chambers form an isolated system so that not only  $d_e Q \equiv 0$  but also that the expansion occurs at *constant* energy  $E^0$ . Therefore,  $d_e W \equiv 0$ . Therefore, the traditional formulation of the first law is of no use in obtaining any useful information about the nature of irreversibility. The initial pressure and temperature of the gas are  $P^0$  and  $T^0$ . As soon as the mechanism is removed, the partition becomes free to move and the gas expands into the other chamber against a zero pressure. The pressure difference  $\Delta P(t) = P(t)$ , where  $P(t)$  is the instantaneous pressure of the expanding gas occupying a volume  $V(t)$ ; the latter can be recorded as a function of time. Using the recorded  $V(t)$ , the temperature  $T(t)$  and  $P(t)$  of the gas are then obtained from the instantaneous equation of state of the gas and the condition  $E(t) = E^0$ . The resulting irreversible work is  $d_i W(t) = P(t)dV(t) \equiv d_i Q(t) = T(t)d_i S(t)$ , where we have used Eq. (16b) with  $d_e S(t) = 0$ . We thus find

$$\Delta_i S(t) = \int_{V^0}^{V(t)} P(t)dV(t)/T(t) = \int_{S^0}^{S(t)} dS|_E(t) = S|_E(t) - S|_E^0,$$

where the suffix  $E$  is used to represent that  $E$  is constant in the process, and where  $S|_E^0$  represents the initial entropy. Neither the initial state nor the state at  $t$  is required to be an

equilibrium state in the above calculation, which follows the recorded non-equilibrium path given by  $V(t)$  at constant  $E$ .

Assuming the initial and final states to be equilibrium states, we have

$$\Delta_i S(t \rightarrow \infty) = S_{\text{eq}}(E^0, 2V^0, N) - S_{\text{eq}}(E^0, V^0, N).$$

For an ideal gas, we evidently obtain  $\Delta_i S(t \rightarrow \infty) = N \ln 2$  between the two equilibrium states, as expected.

The work done by and the heat generated within the system are given by

$$\Delta W(t) = \Delta_i Q(t) = \Delta_i W(t) = \int_{V^0}^{V(t)} P(t) dV(t),$$

and can be calculated for the expansion profile given by  $V(t)$ .

## B. Relative Motion and the Resulting Friction

Let us consider a different situation, in which the system is also moving with respect to the medium with some velocity  $\mathbf{V}(t)$  given by [8, 34]

$$\beta(t)\mathbf{V}(t) = -(\partial S(t)/\partial \mathbf{P}(t))_{E(t), V(t)}$$

in which  $\mathbf{P}(t)$  and  $E(t)$  are the momentum and internal energy of the system in the lab frame (in which  $\Sigma_0$ , and to a very good approximation  $\tilde{\Sigma}$  are at rest). Such a motion arises during sudden mixing of fluids or in a Couette flow, and eventually stops due to deceleration caused by generated frictional forces as a result of the relative motion; we do not consider any external force causing this motion. The irreversible work done by the system against friction is

$$d_i^{\text{fr}} W(t) = -\mathbf{V}(t) \cdot \mathbf{F}_{\text{fr}} dt > 0,$$

where  $\mathbf{F}_{\text{fr}}$  is the resulting frictional force opposing the motion and results in  $d\mathbf{P}(t) \equiv \mathbf{F}_{\text{fr}} dt$ . It is clear that  $d_i^{\text{fr}} W(t)$  vanishes as the motion ceases. This dissipative work is in addition to the irreversible work caused by any pressure difference and any affinity as before:

$$d_i W(t) = (P(t) - P_0) dV(t) + A(t) d\xi(t) - \mathbf{V}(t) \cdot d\mathbf{P}(t). \quad (46)$$

From Eq. (16) and Eq. (8), we then find

$$T(t) d_i S(t) = [(P(t) - P_0) dV(t) + A(t) d\xi(t) - \mathbf{V}(t) \cdot d\mathbf{P}(t) - (T(t) - T_0) d_e S(t)].$$

The same conclusion can also be obtained by considering the Gibbs fundamental relation for this case. Using the above definition of the velocity, it is easy to see that

$$dE(t) = T(t)dS(t) + \mathbf{V}(t) \cdot d\mathbf{P}(t) - P(t)dV(t) - A(t)d\xi(t); \quad (47)$$

see Ref. [8]. The last three terms, being isentropic contribution to  $dE(t)$  represent  $dW(t)$ , while the first term represents  $dQ(t)$ . We now follow Ref. [8] and rewrite

$$dW(t) = P_0dV(t) - \mathbf{V}_0 \cdot d\mathbf{P}(t) + (P(t) - P_0)dV(t) - (\mathbf{V}(t) - \mathbf{V}_0) \cdot d\mathbf{P}(t), \quad (48)$$

with the first two terms representing  $d_eW(t)$ , and the last two terms  $d_iW(t)$ . Here,  $\mathbf{V}_0$  represents the equilibrium pressure velocity. However, the equilibrium value of  $\mathbf{V}(t)$  is  $\mathbf{V}_0 = 0$ , which then yields  $d_iW(t)$  given in Eq. (46). The exchange work  $d_eW(t) = P_0dV(t)$  remains unchanged and says nothing about the presence of internal friction terms that appears in our approach.

## VIII. INCLUSION OF OTHER STATE VARIABLES

Let us now extend the discussion to include other extensive quantities such as the flow of matter, the electric interactions, chemical reactions, etc. For specificity, we focus on chemical reactions, which we assume to be described by a single extent of reaction  $\xi(t)$ . The corresponding affinity for the system is given by  $A(t)$ , while that for the medium is given by  $A_0 = 0$ . We assume another observable  $X$  such as the number of solvent in a binary mixture. The corresponding chemical potential is  $\mu(t)$  for the system and  $\mu_0$  for the medium. The work is now

$$dW(t) = P(t)dV(t) - \mu(t)dX + A(t)d\xi(t). \quad (49)$$

The Gibbs fundamental relation for  $\Sigma$  is given by

$$dE(t) = T(t)dS(t) - P(t)dV(t) + \mu(t)dX - A(t)d\xi(t), \quad (50)$$

while the first law for it takes the form  $dE(t) = dQ(t) - dW(t)$ . Rewriting  $dQ(t) = dE(t) + P(t)dV(t) - \mu(t)dX + A(t)d\xi(t)$  as  $dQ(t) = dE(t) + P_0dV(t) - \mu_0dX + (P(t) - P_0)dV(t) - (\mu(t) - \mu_0)dX + A(t)d\xi(t)$ , we can identify [8]  $d_eQ(t)$  with the first three terms

$$d_eQ(t) = dE(t) + P_0dV(t) - \mu_0dX.$$

The last two terms represent  $d_e W(t)$ :

$$d_e W(t) = P_0 dV(t) - \mu_0 dX,$$

which shows that the second term will appear in the traditional formulation of the first law, but not the associated thermodynamic force  $\mu_0 - \mu(t)$ ; see below. Similarly,  $d_i Q(t)(t) = d_i W(t)$  represents the dissipation given by

$$d_i W(t) = (P(t) - P_0) dV(t) - (\mu(t) - \mu_0) dX + A(t) d\xi(t); \quad (51)$$

see Eq. (8). According to the second law, each contribution in  $d_i W(t)$  is non-negative. The irreversible entropy generation is given by

$$T_0 d_i S(t) = [T_0 - T(t)] dS(t) + [P(t) - P_0] dV(t) + A(t) d\xi(t) + (\mu_0 - \mu(t)) dX(t). \quad (52)$$

The extension to arbitrary number of observables and internal variables is trivial [8].

## IX. A CLOSED SYSTEM PERFORMING WORK ON AN EXTERNAL OBJECT

We now consider our isolated system to consist of the previous medium  $\tilde{\Sigma}(T_0, P_0, A_0)$ , the system  $\Sigma[T(t), P(t), A(t), \mu(t)]$  and an external object  $\Sigma_{\text{ext}}[T_0, P_0, A_0, \mu_{\text{ext}}(t)]$ ; the latter is completely disconnected from the medium but can only exchange the type of work with the system involving the extensive variable  $X(t)$  considered in the previous section. However, there are some important differences. First, we do not limit the external object to be extremely large compared to the system. Accordingly, its chemical potential  $\mu_{\text{ext}}(t)$  can change in time. Just for convenience, we assign to it  $T_0, P_0, A_0$  of the medium, even though it is isolated from the latter and cannot exchange heat and volume and internal variable work with the system and the medium. It is a classic problem that has been extensively studied in which the external object is thermally insulated from the system and the medium; see for example Ref. [34, see Sec. 20 there]. It is also studied by the stochastic trajectory approach; see for example, Refs. [17, 27]. Here, we will closely follow Landau and Lifshitz [34, see Sec. 20 there]. As the external object only performs work, its entropy  $S_{\text{ext}}$  must not change. We will denote the totality of  $\Sigma$  and  $\Sigma_{\text{ext}}$  by  $\bar{\Sigma}$  and all its quantities by an additional bar. For the isolated system  $\bar{\Sigma}$ , we have  $\Delta \bar{S}_0(t) \equiv \Delta_i \bar{S}_0(t) = \Delta [S(t) + S_{\text{ext}}(t) + \tilde{S}(t)] = \Delta [S(t) + \tilde{S}(t)] \geq 0$  during a process involving (not necessarily small) change within the



isolated system  $\bar{\Sigma}_0$ . As usual, all exchange quantities between various pairs of the three parts cancel out for  $\bar{\Sigma}_0$ ; only irreversible quantities survive such as  $\Delta_i \bar{S}_0(t)$ , which in our approach is associated with the entropy generation within  $\bar{\Sigma}$ . Accordingly, we will use the notation  $\Delta_i \bar{S}(t)$  for  $\Delta_i \bar{S}_0(t)$  below and write

$$\Delta_i \bar{S}(t) = \Delta_i S^{(Q)}(t) + \Delta_i S^{(V)}(t) + \Delta_i S^{(\xi)}(t) + \Delta_i \bar{S}^{(X)}(t) \geq 0. \quad (53)$$

The first three terms on the right in the first equation denote the cumulative irreversible entropy changes due to exchanges between the system and the medium and the last term is the cumulative irreversible entropy change due to the exchange between the system and the external object. The work done  $\Delta_e R(t)$  by the external object on the system is

$$\Delta_e R(t) = \Delta [E(t) - T_0 S(t) + P_0 V(t)] + T_0 \Delta_i \bar{S}(t). \quad (54)$$

In terms of  $\Delta_e W(t) = -\Delta_e R(t)$ , we have the following inequality

$$\Delta_e W(t) \leq \Delta G(T_0, P_0, t) \equiv \Delta [E(t) - T_0 S(t) + P_0 V(t)] \quad (55)$$

where  $\Delta G(T_0, P_0, t)$  is the change in the Gibbs free energy of the system. It should be stressed that the above inequality does not assume the establishment of internal equilibrium in the system. If we are considering spontaneous changes occurring within the system in the medium  $\tilde{\Sigma}(T_0, P_0, A_0)$ , we must set the external work  $d_e R = 0$  above by setting  $dX(t) = 0$ . We then find

$$dG(T_0, P_0, t) = -T_0 d_i S(t) \leq 0 \quad (56)$$

during spontaneous relaxation. Thus, assigning the irreversibility to the system leads to the expected behavior of the time-dependent Gibbs free energy of the system.

The corresponding work done by the system with respect to the variable  $X(t)$  is  $dW_X(t) = -\mu(t)dX(t)$ , while the work done by the external object is  $d_e R(t) = \mu_{\text{ext}} dX(t)$ , with the result  $d_i W_X(t) = [\mu_{\text{ext}}(t) - \mu(t)] dX(t) \geq 0$ . We then find

$$T_0 d_i \bar{S}(t) = [T_0 - T(t)] dS(t) + [P(t) - P_0] dV(t) + A(t) d\xi(t) + [\mu_{\text{ext}}(t) - \mu(t)] dX(t) \geq 0, \quad (57)$$

in which the first three terms refer to irreversible entropy generation within the system and the last term refers to the generation within  $\bar{\Sigma}$ . Each term on the right must be non-negative; compare with Eq. (15). Comparison with Eq. (51) shows that the last three terms above represent  $d_i W(t)$ , except that  $\mu_0$  is replaced by  $\mu_{\text{ext}}$ . The additional thermodynamic force

$\mu_{\text{ext}}(t) - \mu(t)$  vanishes when there is equilibrium established between the system and the external object; let the equilibrium value be given by  $\bar{\mu}_0$ . The new force generates the irreversible entropy  $d_i \bar{S}^{(X)}(t)$  due to  $X$ . Following the arguments given in Ref. [8], see Sec. XI there, for the case of thermal equilibration and which can be adapted here verbatim, we find that the irreversible entropies for  $\Sigma$  and  $\Sigma_{\text{ext}}$  are given, respectively, by

$$T_0 d_i S^{(X)}(t) = [\bar{\mu}_0 - \mu(t)] dX(t), T_0 d_i S_{\text{ext}}^{(X)}(t) = [\bar{\mu}_0 - \mu_{\text{ext}}(t)] dX_{\text{ext}}(t), \quad (58)$$

with  $dX(t) + dX_{\text{ext}}(t) = 0$ . As the entropy of the external object remains constant, there must be a corresponding change  $d_e S_{\text{ext}}^{(X)}(t) = -d_i S_{\text{ext}}^{(X)}(t)$  as it performs work, which requires  $d_e p_{k,\text{ext}}(t) = -d_i p_{k,\text{ext}}(t)$  for the  $k$ -th microstate of the object.

If the object is extremely large compared to the system so that the coupling with the system will not appreciably affect  $\mu_{\text{ext}}$ , the latter can be taken as a constant equal to  $\mu_0 = \bar{\mu}_0$ . In this situation, the entire contribution  $d_i \bar{S}^{(X)}(t)$  must be treated as  $d_i S^{(X)}(t)$  assigned to the system, as there is no force in the object to generate irreversibility ( $d_i S_{\text{ext}}(t) = 0$ ).

The difference between our approach and the stochastic trajectory approach should be pointed out. In the latter approach,  $T = T_0$  and  $P = P_0$  for the system. Also, as no internal variable is considered, we will set  $A = A_0 = 0$  above. Thus, the only irreversibility is due to the possibility of work by the external object. The entropy  $S(t)$  is given by the Gibbs formulation; see Eq. (21), and its changes  $dS(t)$  includes the irreversible entropy changes  $d_i S(t) = d_i S^{(X)}(t)$ . This is not the case in the stochastic trajectory approach in which the irreversible entropy  $\Delta_i \bar{S}^{(X)}(t)$  is assigned to the medium [42].

## X. SUMMARY AND DISCUSSION

### A. Summary

The traditional formulation of the first law has two basic deficiencies. The first one is that even though the first law is about the change in the energy of the system, it contains the fields of the medium and not of the system. The second, and more dramatic conceptually, deficiency is that it remains satisfied even if the process violated the second law. This is why both laws are needed in nonequilibrium thermodynamics. Despite the concern expressed by Kestin [12, Sect. 5.12], we have shown that the definition of the generalized heat  $dQ(t)$ , which includes its irreversible component  $d_i Q(t)$ , follows *uniquely* from the unique choice of

$dW(t)$  resulting from the second law, see Eq. (19), and also from the statistical approach, see Eq. (25). In general, we have the identity  $d_iW(t) \equiv d_iQ(t)$  between their irreversible components; see Eq. (8). These results do not require the system to be in internal equilibrium. The situation becomes very illuminating when the system is in internal equilibrium. In this case, the generalized heat formulation gives rise to not only the simple relationship  $dQ(t) = T(t)dS(t)$ , but also the extension of the adiabatic theorem for nonequilibrium states; see Theorem 7. Another remarkable consequence is that in terms of generalized  $dQ(t)$ , the Clausius equality (40) is always maintained, in contrast to the inequality (43) in the traditional approach. Our generalized formulation brings about a symmetry between the system and its surrounding medium, see Eq. (19), which is absent in the traditional approach using external fields. The first law becomes identical to the second law so that we only deal with equalities and a single law; the equalities are easier to deal with than the inequalities that result in the traditional approach; see for example, Eq. (45) or Eq. (7).

The introduction of microstate probabilities and the partition of  $dp_i(t)$  into  $d_e p_i(t)$  and  $d_i p_i(t)$  provide a very convenient and useful statistical representation of exchange and irreversible forms of heat and entropy and of other quantities, and which allows us to draw some useful conclusions. For example, it follows directly from Theorem (7) that pure work cannot change the entropy. This was used to argue that  $S_{\text{ext}}$  must be a constant in Sec. IX. We have found that the microstate probability  $p_i(t)$  is very different from its equilibrium analog  $p_{i,\text{eq}}$ . Several examples have been given to show the usefulness of the new definition of heat and work. Below we list some of the benefits of the new formulation.

## B. Benefits of the Generalized Formulation

1. It is a new way to write the first law, which shows that the first and the second laws are *no longer* independent, a property now shared by all irreversible processes and not just by reversible processes. This conclusion must be contrasted with the well-known result found in all text books and the literature that the two laws are independent for irreversible processes.
2. Work and heat can be uniquely distinguished so that each has a clear physical significance, but no such clear identification is possible in the traditional formulation of the first law; see Theorems (3) and (4).

3. Work and heat no longer are restricted to flow through the boundary. Thus, the new formulation can easily accommodate interactions described by fields (electromagnetic, gravitational, etc.) [12].
4. The entire thermodynamics and stability considerations for any body can be expressed in terms of the variables associated with the body alone at each instant. We can use the instantaneous equations of state of the body alone for thermodynamic computation. Indeed, it may be the only way to study a non-equilibrium system in some cases as is clearly shown by the example of free expansion in Sect. VII. Here, the traditional formulation of the first law is of no use to determine  $d_iW(t)$  and  $d_iS(t)$  as is well known.
5. We deal with equalities and not inequalities. In addition, we only deal with  $dS(t)$ , which as a dependent variable is expressed in terms of state variables  $\mathbf{Z}(t)$ ; there is no need to consider its parts  $d_eS(t)$  and  $d_iS(t)$  separately, which depend on the medium; see (3) in Sect. IID. The generalized heat  $dQ(t)$  and work  $dW(t)$  differ from  $d_eQ(t)$  and  $d_eW(t)$ , respectively, by the same contribution  $d_iQ(t) \equiv d_iW(t) \equiv d_iW_0(t)$ .
6. The use of the Gibbs fundamental relation makes it almost trivial to identify the irreversible contributions. Thus, the new formulation does not have the limitation inherent in the traditional formulation; see (7) in Sect. IID. The determination of  $d_iW_0(t)$  is straightforward by measuring  $P(t)$  and  $P_0$ . Adding this to  $d_eQ(t)$  then allows us to determine  $dQ(t)$ .
7. The most useful aspect of the generalized approach is that the work  $dW(t)$  does not depend on the amount and nature of dissipation going on during a process. It is determined by the instantaneous pressure of the system, which itself is a derivative of its instantaneous entropy, a state variable. We have already seen this earlier in Eq. (12). Whether friction between the piston and the walls is present or not,  $d_iW(t)$  is always given by  $\Delta P(t)dV(t)$  so that  $dW(t) = P(t)dV(t)$ .
8. Once  $dQ(t)$  is known,  $dS(t) \equiv dQ(t)/T(t)$  is also known or vice versa as if we are dealing with a system in equilibrium, even though we are dealing with an out-of-equilibrium system in internal equilibrium. In the latter situation, the analysis is considerably simplified as we are always dealing with the instantaneous properties such

as the equation of state of the system even though the system is out of equilibrium.

We do not need to, or may not, know these properties for  $\tilde{\Sigma}$ .

The new formulation has many other desirable properties. The generalized heat  $dQ(t)$  and work  $dW(t)$  differ from  $d_e Q(t)$  and  $d_e W(t)$ , respectively, by the same contribution  $d_i Q(t) \equiv d_i W(t)$ . The determination of  $d_i W(t)$  is straight forward in terms of thermodynamic forces  $P(t) - P_0, A(t)$ , etc. Adding this to  $d_e Q(t)$  then allows us to determine  $dQ(t)$  from which  $dS(t)$  can be determined.

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